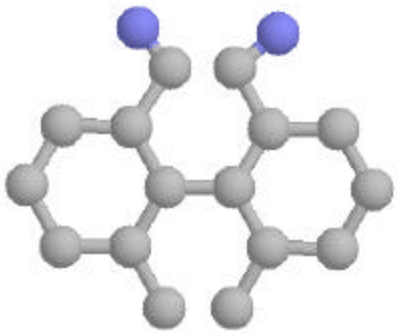
Chemistry 361B **NAME_____KEY_____**
Spring 2002
Quiz 3
40 points

This is a closed book quiz, no notes allowed. You will have ten minutes to answer the following question.

1. (20 points) Consider the molecule 2,2'-dimethyl-6,6'-dicyanobiphenyl:



This molecule is described in your textbook in Figure 18.3. In the figure here, the hydrogens have been omitted for clarity from the aromatic rings and the two methyl groups.

(a) (8 points)What is the point group of this object in BOTH Hermann-Mauguin and Schoenflies notation? You will not receive full credit unless you give the point group in BOTH notations.

This molecule has a 2-fold axis of rotation, which superimposes left to right and vice versa. This axis is in the plan of a mirror that reflects left to right and vice versa. There is also a mirror in the plane of the molecule and which contains this axis. Therefore, this molecule belongs to the same point group as water. In H-M notation this would be 2mm. In Schoenflies notation, this is C2v.

(b) (6 points) Clearly label the symmetry elements using correct symbols.

(c) (6 points) Would this molecule be optically active? Why or why not?

This molecule is NOT optically active, because it does not contain any asymmetric (chiral) centers.

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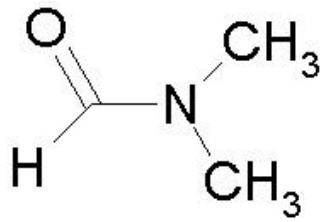
2. (20 points) In case you need some equations for this NMR problem,

$1T = 10^4$ gauss
$B_0 = 2\pi\nu/g$
$\gamma/10^7\ T^{-1}s^{-1}$ for $^1H = 26.75$
ν/MHz for ^1H in 4.7 T field = 200
$E_I = -m_I B_0 \gamma h/2\pi$
^1H I = ½
$N_1/N_0 = \exp(-\Delta E/k_B T)$ Boltzmann distribution
$h = 6.626 \times 10^{-34}$ J-s
$k_B = 1.381 \times 10^{-23}$ JK^{-1}
$\delta = [(\nu - \nu_{ref})/\nu_{ref}] \times 10^6$

(a) (4 points) Consider the molecule N,N'-dimethylformamide:



At 25C, the NMR spectrum shows two methyl peaks. At 130C, there is only one peak due to the methyl protons. Explain.

This is problem 17.62 in your text. At higher temperature, the rotation about the C-N bond becomes rapid enough to average out the chemical environment and thus the chemical shifts of the two methyl groups.

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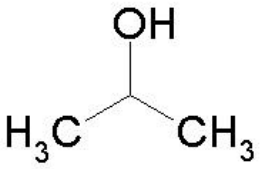
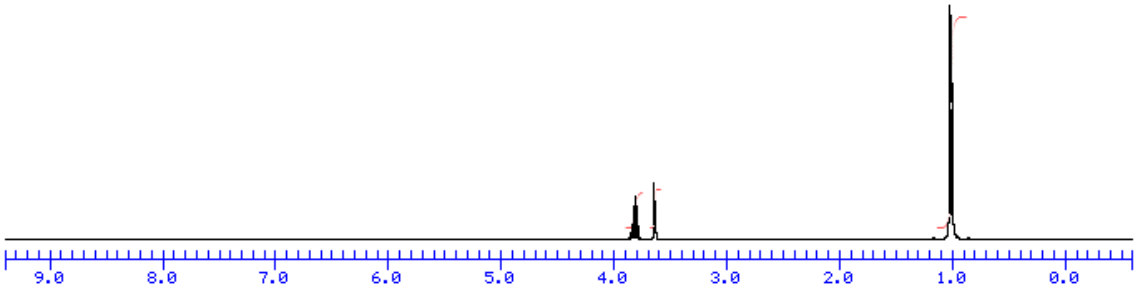
(b) (8 points) Consider the molecule isopropanol:



Sketch its *qualitative* ^{1}H NMR spectrum, identifying the type of proton giving rise to each peak, and indicating any splitting that would occur and why. You do not have to provide exact chemical shifts, only the relative chemical shifts for each type of proton you identify.

The upfield peak is a doublet, the downfield peak is a septet, the midpeak is more or less a singlet, somewhat broad. The septet belongs to the CH proton, linked to the –OH. This is split by the six equivalent methyl protons. The hydroxyl proton is the midpeak. The upfield peak belongs to the methyl protons.



(c) (8 points) Suppose the NMR spectrum of isopropanol is recorded at 200 MHz and 400 MHz. Indicate whether each of the following remains unchanged (U) or is different (D) at 200 MHz and 400 MHz and give a short, one-sentence reason why:

(i) sensitivity of detection __D__

more favorable Boltzmann distribution

(ii) $|\delta_{CH3} - \delta_{OH}|$ __U__

The chemical shifts would change by the same amount with a change in frequency.

(iii) $|\nu_{CH3} - \nu_{OH}|$ __D__

The resonance frequencies themselves would change, and this difference would actually be larger.

(iv) J __U__

The spin-spin coupling would not change.